

## Successful formation of uniform organic thin films of macroscopic size by rational space-filling design

Thin film is an important form of materials for many practical applications. The perfect control of the orientation and alignment of constituent molecules in organic films would realize maximal utility of the intrinsic nature of the molecules, thus leading to the development of high-performance organic materials and devices [1-3]. However, it is extremely difficult to fabricate organic films that have a uniform structure over large areas. One of the general reasons is that when molecules assemble on a substrate, the nucleation and growth of assemblies take place at various locations, resulting in the formation of many nanometer-size domains, which are usually oriented randomly on the substrate. The domain boundaries severely degrade the properties of films in terms of, for example, mechanical strength and electrical conduction. To solve this problem in the fabrication of organic films, we recently devised a rational strategy and successfully constructed largearea thin films devoid of domain boundaries using a newly designed molecular building block [4].

Our strategy for achieving large-area uniform thin films is based on a space-filling design of a "2D + 1D" assembly (Fig. 1(a)), which is inspired by the structure of graphite consisting of atomic 2D hexagonal arrays of carbon. We conceived that a three-bladed propeller-shaped molecular building block could form a one-dimensional (1D) stacking structure of twodimensional (2D) hexagonal arrays (Fig. 1(a)). Such propeller-shaped molecules mesh like gears to form nested hexagonal packing, which is an ideal motif for the tessellation of the 2D plane. Furthermore, translational and rotational motions, which are possible factors behind the formation of domain boundaries, would be limited in the nested packing of the propeller units. The construction of this kind of two-dimensional sheet may facilitate regular packing in a three-dimensional (3D) space by vertical stacking (Fig. 1(a)). We expected that this space-filling design would be realized using a particular type of triptycene, which is a propeller-shaped rigid molecule comprising three phenylene rings. On the basis of the above idea, we synthesized a series of tripodal triptycenes such as **Trip** (Fig. 1(b)), to which three paraffinic side chains are regiospecifically introduced.

To elucidate the assembly structure of Trip, we performed powder X-ray diffraction (XRD) analysis of a bulk sample of Trip using synchrotron X-ray radiation at BL44B2 and BL45XU, in collaboration with Dr. Takaaki Hikima and Dr. Masaki Takata (RIKEN). The obtained XRD pattern showed that Trip indeed formed a 2D sheet structure by nested packing, which aligns one-dimensionally to form a 1D lamellar structure (Fig. 2(a)). We successfully fabricated a uniform film simply by sandwiching a powder sample of Trip between sapphire substrates, heating it to its isotropic hot melt (215°C), and slowly cooling (0.5°C/min) it to 25°C (Fig. 2(b)). The resulting crystalline film showed an entirely dark image in the polarized optical microscopy observation, indicating the formation of a highly oriented assembly. Interestingly, the throughview XRD image of this crystalline film clearly showed hexagonally arranged diffraction spots originating from the 2D hexagonal lattice (Fig. 2(c)), while diffractions arising from the 1D lamellar structure were not detected. These observations indicate that a 2D layer structure uniformly develops parallel to the substrate. Importantly, the domain size of the assembly is larger than the X-ray beam size  $(350 \times 150 \,\mu\text{m}^2)$ . To our surprise, the throughview XRD patterns, obtained at more than 30 different points of the crystalline film, showed hexagonally



Fig. 1. (a) Schematic representation of a space-filling model with a three-bladed, propeller-shaped motif that forms a 2D hexagonal array by nested packing. 1D stacking of the 2D hexagonal leads to a layered structure with high structural order. (b) Molecular structure of tripodal paraffinic triptycene **Trip** that embodies the space-filling design.



Fig. 2. (a) 1D powder XRD profile and schematic representation of the assembly structure (inset) of a bulk sample of **Trip** at 30°C upon cooling from its isotropic hot melt in a glass capillary. (b) Photograph of a large-area crystalline **Trip** film sandwiched by sapphire substrates. (c) Through-view XRD image of the large-area crystalline **Trip** film. Values in parentheses are Miller indices.

arranged diffraction spots with identical orientation to one another, thus demonstrating that this **Trip** film is devoid of domain boundaries at the centimeter length scale. The fabrication of domain-boundary-free film at this scale is the equivalent of regularly paving the entire surface of the *Eurasia* continent with 1.8 m<sup>2</sup> tiles.

Trip can be vacuum-deposited onto various substrates, affording uniform thin films. Grazingincidence X-ray diffraction (GI-XRD) analysis at BL45XU clearly showed that the evaporated 50-nmthick film of Trip on a silicon substrate has a completely oriented "2D + 1D" structure (Fig. 3(a)). Furthermore, the through-view XRD pattern of the evaporated film on a sapphire substrate (Fig. 3(b)) displayed hexagonally arranged short arcs (Fig. 3(c)), indicating that the 2D nested hexagonal triptycene arrays in the film are aligned to some extent. By measuring the XRD images at different points of the film at least one centimeter apart, this evaporated film was found to have no detectable domain boundaries. The GI-XRD images observed for the evaporated 50-nm-thick films of Trip, fabricated on polyimide (PI), polyethylene terephthalate (PET), quartz, and mica, are essentially identical to one another. Therefore, even in assembly from the vapor phase, Trip can exhibit its extraordinary 2D structuring capability.

In summary, the space-filling design using a simple tripodal triptycene building block allows the formation of 2D arrays with extraordinary long-range structural integrity. The 2D arrays pile up next to one another to give a "2D + 1D" structure, resulting in the formation of completely oriented, domain-boundary-free molecular thin films with a size beyond the centimeter length scale. The tripodal triptycenes may serve as useful building blocks for the development of functional thinfilm materials [5].



Fig. 3. (a) Schematic representation of the assembly structure of **Trip** (top) and a 2D GI-XRD image of a 50-nm-thick evaporated film of **Trip** on a silicon wafer. (b) Photograph of a 50-nm-thick evaporated film of **Trip** on a sapphire substrate. (c) Through-view XRD image of the evaporated **Trip** film on a sapphire substrate. Values in parentheses are Miller indices.

1 cm

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